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DINITROTOLUENE (DNT)-FREE SINGLE BASE PROPELLANT

BACKGROUND OF THE INVENTION

I. Field of the Invention

The present invention relates generally to single base propellants and, more particularly, to the reduction of environmental hazards by the elimination of the need to incorporate dinitrotoluene (DNT) in single base propellants. The invention provides substitute, less energetic but more efficient, plasticizing compounds which enable the incorporation of additional relative amounts of nitrocellulose (NC) in the mix thereby maintaining overall energy levels.

II. Related Art

Single base propellants generally contain colloided nitrocellulose powders as the chief energetic component and this makes up about 85-99% (weight) of the propellant mix. The nitrocellulose is combined with a plasticizer to give the mix the desired mechanical properties so that the material can be processed into grains or other shapes utilized in, for example, 155 mm Artillery charges or 120 mm tank ammunition, or for other projectile firing purposes. Varying amounts of other stabilizing additives are added to the mix to reduce hazards sensitivity and to prolong shelf life. Double or multi base propellants, on the other hand, contain the same colloided nitrocellulose component, but utilize a second, liquid energetic compound such as nitroglycerin (NC) or an equivalent energetic liquid nitrate ester as a plasticizer. A third energetic component is also added in triple based composition. Double base powders typically contain about 80% colloided nitrocellulose with the major portion of the remaining material consisting of the nitroglycerin fraction. The powders of the present invention are single base propellants. They must be relatively hazard insensitive

and so avoid shock or heat sensitive plasticizers. An example of a prior blasting composition using NC and DNT is shown in U.S. Patent No. 3,328,217.

Most single base propellants traditionally contain a significant amount of dinitrotoluene (DNT) which acts as a plasticizer for the nitrocellulose to impart the desirable mechanical properties to the mix which, in turn, facilitate the processing of the mix into grains and other shapes utilized, for example, in the manufacture (loading) of large caliber cartridge munitions such as 155 mm Artillery charges or 120 mm tank ammunition. Such single base propellants normally contain from about 1-10% DNT which itself is an energetic plasticizer albeit of low hazards sensitivity. In addition to being an energetic plasticizer, DNT also reduces the hygroscopic properties of the nitrocellulose making the mixture more water resistant and can be used to adjust the burning rate as it reduces the burning rate of pure nitrocellulose.

Single base propellants are produced utilizing a solvent-type process. An example of which is found in U.S. Patent No. 4,525,313 to Muller. Ingredients are mixed utilizing volatile solvents or gelling agents which, as a rule, are selected from ketones, alcohols, ethers or mixtures thereof. The use of such solvents in combination with thermoplastic shaping processes including pressing and extruding equipment enable forming to take place at relatively low working temperatures. For example, nitrocellulose that has been turned into a doughy mass can readily be extruded in desired shapes at <50°C. The use of DNT lends itself readily to such a process inasmuch as that component can be in the form of an oil, solid or an oil-solid mixture which includes all three DNT isomers (i.e., 2,4;2,5 and 2,6 DNT) and generally freezes in the range from about 20-35°C. The solid form is generally para or

2,4-dinitrotoluene. This material also lends itself readily to solvent processing with the nitrocellulose.

DNT has had a long and successful use as the major plasticizing and energy adjustment component in single base propellants and, with respect to the properties of the propellants themselves, has been quite successful. The DNT is normally utilized with an amount of a second plasticizer, generally dibutylphthalate (DBP) which works well in combination with the DNT.

Thus, those skilled in the art appreciate that dinitrotoluene (DNT) has many attributes which make it a successful plasticizer and energy adjustment material for single base propellants. While successful from the standpoint of processing and use of the propellant, DNT carries with it significant environmental drawbacks which have more recently provoked increasingly important concerns. Fine particulate DNT is considered quite toxic as when dust is produced in de-milling propellant. Residue DNT has traditionally been burned to destroy the material, but this produces undesirable nitrogen oxides (NO_x). Polycyclic aromatics (PAH's) are also given off by the combustion of DNT and these are considered quite carcinogenic. In addition, DNT is soluble up to about 150 PPM in water so that this presents a serious potential waste water problem. The material has not only been classified as a potential carcinogen, but also has been declared a hazardous waste by the EPA.

The dangers associated with use of DNT plasticizers has required high cost, personal protective equipment to be worn by those working with the material and expensive precautions to be taken with respect to containment and treatment of contaminated materials such as waste water containing DNT. Thus, there has long been a need in the manufacture of such single base propellants to provide a

non-toxic and environmentally safe chemical to replace the DNT plasticizer without sacrificing performance in the propellant material and which can be processed with existing production equipment for single base propellants.

In addition to DNT, dibubylphthalate (DBP) is also present in many plasticizer systems for NC single base propellant compositions in lesser amounts, normally 2-5%. While not necessarily as undesirable as DNT, DBP is also considered a toxic material. It would also be advantageous to eliminate this material from the compositions as well.

Furthermore, diphenyl amine (DPA) which is the most common stabilizer used in single-base propellants also presents a potential environmental hazard. DPA is on the Enviromental Protection Agencies Toxic Releases Inventor (TRI) list.

Accordingly, it is a primary object of the present invention to provide a single base propellant which does not require DNT as a modifier or plasticizer material.

Another object of the invention is to provide a single base propellant which does not contain DNT but which can be processed using existing single base processing equipment.

Yet another object of the invention is to provide a single base propellant which does not require DBP in the formula.

An additional object of this invention is to provide a single base propellant which does not use DPA as the stabilizer.

A further object of the present invention is to provide non-toxic and environmentally friendly chemical plasticizers for single base propellants that do not require DNT, DBP or DPA.

It is a yet still further object of the present invention to provide non-toxic and environmentally friendly plasticizers for single base propellants, the incorporation

of which does not result in an overall lowered performance of the propellant.

A yet still further object of the invention is to provide new plasticizers for single base propellants which are non-toxic and environmentally safe and which can be added to the propellant utilizing the same processing solvents used for other components in existing single base processes.

Other objects and advantages of the invention will become apparent to those skilled in the art upon becoming familiar with the present specification and appended claims.

SUMMARY OF THE INVENTION

The present invention provides viable environmentally friendly substitutes for dinitrotoluene (DNT) in single base munition propellants which are compatible with existing solvent-type single base propellant manufacturing processes and which, in addition, enable propellants compatible in performance to existing DNT-containing loads.

In accordance with the present invention, it has been discovered that certain adipate and citrate compounds can be used in relatively small quantities to sufficiently plasticize high nitrogen (N) (about 13.2% N) nitrocellulose (NC) in single base propellants. The required relative quantities are far less than that required using DNT, i.e., about 2-5% versus about 7-10% or more of DNT. Although, unlike DNT, these compounds are not energetic themselves, and thus, actually have a negative energy output with respect to the propellant compared to the positive energy of DNT, the lesser required amounts allow corresponding increases in the allowable percentage of NC in the propellant mix which offsets the negative energy of the plasticizers of the invention and results in an overall comparable energy yield for the propellant, typically

impetus levels of up to 986 J/g.. This is comparable to prior DNT containing loads such as M14 utilized for 120 mm tank cartridges.

The preferred compounds in accordance with the invention include certain adipate and/or citrate compounds including diisobutyl adipate (DIBA), diisooctly adipate (DIOA), acetyltriethyl citrate (ATEC), acetyltri-n-butyl citrate, triethyl citrate and tributyl citrate. Exemplary propellant compositions include from about 94-96% high N nitrocellulose (about 13.2% N), about 2-4% plasticizer and the remainder dibutylphthalate (DBP). The DBP provides additional plasticizing qualities. In addition, a small amount, nominally 1%, diphenylamine (DPA) is added to the mix as a thermal stabilizing material.

Additional embodiments include up to about 10% or more ATEC and no DNT or DBP. These compositions contain a lesser amount of high N nitrocellulose (about 88-90%). These formulations may also contain ethyl cellulose as the stabilizer in place of the DPA. These compositions containing approximately 10% of the new plasticizer system result in lower energy levels that are comparable to currently produced Artillery propellants such as M1, or approximately 930 J/g impetus.

The propellant combination of the invention containing the environmentally friendly plasticizing materials can be processed using conventional single base solvent processing techniques including conventional solvents, presses, extrusion and cutting devices and solvent recovery techniques.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

Figure 1 shows the accelerated aging properties of certain new compositions according to the invention relative to M14; and

Figure 2 depicts ballistic test results using a Gamma Dynagun for a composition of the invention with M14 energetics.

DETAILED DESCRIPTION

In accordance with the invention, improvements have been made in single base propellant compositions which enable them to be more friendly to those engaged in the manufacturing processes and more compatible with the environment. This has been accomplished, for the most part, by eliminating dinitrotoluene (DNT) from single base propellants which is a component that has possessed attributes with regard to enhancing propellant properties but which, at the same time, has presented both a hazard to the people engaged in the manufacturing process and an environmental menace from the standpoint of creating hazardous waste materials in effluents, particularly when burned (as poly aromatic hydrocarbons) and in waste water. According to the invention, there have been discovered certain plasticizing compounds which enable substitution for DNT without sacrificing overall propellant performance. These compounds can sufficiently plasticize high N nitrocellulose (NC) sufficiently to enable proper processing into grains suitable for use in large caliber munitions, particularly, 155 mm Artillery charges and 120 mm tank ammunition.

Thus, it has been discovered that certain citrate and adipate compounds successfully plasticize high N nitrocellulose (NC) in single base propellant systems utilizing sufficiently low percentages of these non-energetic materials such that additional percentages of NC can be incorporated in the formula thereby maintaining the overall energy output substantially constant.

It should be noted that a variety of materials have been evaluated in this regard including adipates and

citrates, phthlates, polycaprolactones, ureas, urethanes and other materials. Attributes desired and evaluated include ability to plasticize NC, toxicity, processing/physical characteristics (compatibility with single base processing solvents and equipment) and mechanical characteristics imparted to the mix, prior usage in propellants, energetic qualities, availability and cost. As previously noted, DNT has a long history of successful prior usage and its ability to plasticize NC and create processible physical characteristics in the mix. DNT, of course, is moderately energetic and the presence of larger percentages of it does not reduce the overall energy output of the propellant material. Thus, it was quite unexpected that DNT could be replaced using a low or negative energy material without sacrificing the overall performance of the mix.

In accordance with the invention, it has been discovered that a number of citrate compounds, together with at least one adipate successfully meet the necessary criteria for substituting for DNT in single base munition propellants. Thus, according to the present invention, it has been found that diisobutyl adipate (DIBA) available, for example, as Plasthall DIBA from the C.P. Hall Company, Memphis, Tennessee, acetyltriethyl citrate (ATEC) available as Citroflex® A-2 from Morflex, Inc., Greensboro, North Carolina, and acetyltri-n-butyl citrate available as Citroflex A-4 also from Morflex, Inc. were especially successful. Other citrates, including triethyl citrate, available as Citroflex 2, and tributyl citrate, available as Citroflex 4, both from Morflex, Inc., of Greensboro, North Carolina, were also usable.

According to the invention, then, it has been discovered that DNT-free single base propellants containing from 2-10% by weight of these new plasticizers display the

desirable ballistic, mechanical, thermochemical and stability properties of standard DNT-containing propellant formulations. An important property of these plasticizers is that they can be added to the propellant in a standard pre-mixed form with the processing solvents typically used in single base processes. The plasticizers are relatively non-toxic and are environmentally acceptable under current governmental regulations.

The processing solvents for processing single base propellants include conventional solvents for NC which vary depending on the N content of the nitrocellulose. Thus, high grade nitrocellulose which has above about 13.15% N is practically insoluble in ether, but is readily dispersed by plasticizers and acetone. Below about 13.15% N, either can be used. In some cases, combinations of acetone or ether and other solvents such as alcohols or other ketones are preferred.

In any event, in normal solvent-type processing, solid blocks of NC are broken and blended into the solvent together with an amount of the desired plasticizing agent, which is added or blended in from a slurry utilizing common solvents. Additional stabilizing materials are added prior to final mixing of the solubilized/plasticized nitrocellulose. The ability to add the plasticizers dispersed in a common solvent or solvents, of course, improves the uniformity of the mix and reduces the time of the mixing cycle. In addition to the other ingredients, if more solvent is needed, this is added to the material in the final mix or possibly in stages during the mix. After all the ingredients have been added to the mixer, the mix cycle continues for a given period of time, possibly 1 hour, until the single base propellant is thoroughly mixed.

After the mixing operation has been completed, the mixed propellant is dried by removal and recovery of some

of the solvent from the mixed batch until a desired level of plasticity is achieved. Adjustment procedure steps, including drying and adding solvent, may continue until the correct plasticity is achieved and thereafter the mixer is run for a short time to allow the solvent to equalize throughout the mix.

After mixing has been completed and the proper solvent level reached, the material is transferred to a blocking press where it is subjected to a high pressure hydraulic ram to pressurize the material to remove occluded air, improve consolidation and form the blocks into the proper shape for the graining press.

The blocked material is then transferred to the graining press. In the graining press, various techniques are utilized to extrude strands of propellant depending on the desired final configuration or use. The strands of propellant are cut to a specified length for further drying prior to final cutting into actual grain length.

The extruded material is dried in a manner which saves and recovers as much solvent as is practical for reuse and so the first step is normally to process the load in a solvent recovery tank. The material is then subjected to a water-dry operation where additional solvents are extracted into the water and thereafter to an air-dry cycle where the surface moisture is removed. Processing of the new compositions may also be accomplished in new continuos processes where the batch operations are replaced by continuous mixers, extruders and solvent removal.

Having presented an overview of the invention, additional information with respect to certain specific examples, which are intended to exemplify rather than to limit the scope of the invention, will next be presented. Much of the information is in the form of tabular data criteria which will be familiar to those skilled in the

art.

Table 1 shows a prior formulation utilizing dinitrotoluene (DNT) as the principle plasticizer and energy adjustment compound. The composition is an example of a mix generally known as M14 and nominally contains about 8% DNT. Note that the specific example contained 8.29% DNT and 2% DBP.

TABLE 1

M14 PROPELLANT COMPOSITION

CONSTITUENT	PERCENT FORMULA	
NITROCELLULOSE	90.00	
DINITROTOLUENE	8.00	
DIBUTYLPHTHALATE	2.00	
TOTAL	100.00	
DIPHENYLAMINE (ADDED)	1.00	
MOISTURE	0.6	
RESIDUAL SOLVENT	0.7	
GRAPHITE GLAZE	0.2	

Table 2A shows three examples (Example 1, Example 2 and Example 3) of percentage compositions formulated in accordance with the present invention in which lesser amounts of the material known as plasticizer "340" has been substituted for the DNT fraction and the percentage of NC increased. The material known as plasticizer "340" is diisobutyl adipate or (DIBA) available as Plastall DIBA from the C.P. Hall Company.

TABLE 2A

PROPELLANT COMPOSITION				
		EXAMPLE 1	EXAMPLE 2	EXAMPLE 3
CONSTITUENT	PERCENT FORMULA	PERCENT MEASURED	PERCENT MEASURED	PERCENT MEASURED
NITROCELLULOSE	96.00	96.23	96.09	96.14
PLASTICIZER "340"	2.10	1.95	2.01	1.99
DIBUTYLPHTHALATE	1.90	1.82	1.90	1.87
TOTAL	100.00			
DIPHENYLAMINE	1.00	0.97	1.00	0.98
MOISTURE	0.6	0.7	0.6	0.6
RESIDUAL SOLVENT	0.7	0.9	0.8	0.5
GRAPHITE GLAZE	0.2	0.1	0.1	0.1

TABLE 2B

PROPELLANT COMPOSITION		
		EXAMPLE 4
CONSTITUENT	PERCENT FORMULA	PERCENT MEASURED
NITROCELLULOSE	95.00	95.04
PLASTICIZER "340"	3.10	3.08
DIBUTYLPHTHALATE	1.90	1.88
TOTAL	100.00	
DIPHENYLAMINE	1.00	1.08
MOISTURE	0.6	0.5
RESIDUAL SOLVENT	0.7	0.5
GRAPHITE GLAZE	0.2	0.1

Table 2B depicts an additional example, Example 4, in which the DNT fraction is replaced by a lesser amount of a material known as plasticizer "319", which is acetyltriethyl citrate, purchased as Citroflex A-2 from Morflex, Inc.

The stability and physical test result with respect to Examples 1-4 and which correspond to the tests conducted for the prior art DNT-containing material M14 are shown in Table 3. From this it can be seen that the hygroscopicity is slightly higher owing to the superior hygroscopicity reducing properties of DNT, in larger quantities. Percentages in Examples 1-4, however, are still within tolerable limits and, as can be seen from the remainder of Table 3 and from the closed bomb testing of Examples 1-4 described in Table 4, that the performance and stability of the DNT-free material is comparable to that of M14.

TABLE 3

STABILITY AND PHYSICAL TEST					
		EXAMPLE 1	EXAMPLE 2	EXAMPLE 3	EXAMPLE 4
TEST	FORMULA	ACTUAL	ACTUAL	ACTUAL	ACTUAL
HEAT TEST SP. 134.5 Deg. C	NO CC 40'	CC 60+	CC 60+	CC 60+	CC 60+
NO EXPLOSION	5 Hrs MIN	NE 5 HRS	NE 5 HRS	NE 5 HRS	NE 5 HRS
FORM OF PROPELLANT	CYLINDRICAL	CYL	CYL	CYL	CYL
NUMBER OF PERFS	19	19	19	19	19
BULK DENSITY, LBS/CUFT	INFO	52.29	50.37	48.19	50.78
HOE,cal/g	INFO	855.1	858.2	864.6	854.3
HYGROSCOPICITY, %	INFO	0.99	1.00	1.09	0.98
ABSOLUTE DENSITY,G/CC	INFO	1.54	1.56	1.51	1.5
WT. UNIFORMITY (100 Grains). G	INFO	140.5	100.8	65.0	121.3

TABLE 4

CLOSED BOMBS									
		EXAMPLE 1		EXAMPLE 2		EXAMPLE 3		EXAMPLE 4	
	TEMP Deg. F	RELATIVE QUICKNESS	RELATIVE FORCE	RELATIVE QUICKNESS	RELATIVE FORCE	RELATIVE QUICKNESS	RELATIVE FORCE	RELATIVE QUICKNESS	RELATIVE FORCE
TEST	+90	85.9	98.4	91.3	98.9	103.8	99.7	85.9	98.4
	-40	82.3	98.2	86.2	98.5	97.3	97.7	82.3	98.2
	+145	92.9	100.9	97.5	100.7	107.7	101.6	92.9	100.9
STD	+90	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Figure 1 shows the accelerated aging properties of the new composition(s) relative to M14 at 150° F. Results of the long term aging show that these formulations age at a comparable rate to the standard M14 propellant.

Figure 2A shows ballistic test results from the Gamma Dynagun for the new composition with M14 energetics. The Gamma Dynagun is an interior ballistics test device based on a 105 Howitzer that allows assessment of required charge weights to obtain comparable muzzle velocities and pressures to a standard propellant lot. It can be seen

from Figure 2 that the charge weight of the new composition is within the same statistical population as the standard M14 propellant lot and a number of production lots of M14.

As can be seen from the description and examples herein, it is now possible to replace the DNT fraction in propellant materials such as M14 without sacrificing other desirable propellant properties. The use of other materials, particularly citrate and adipate compounds, is also promising. Note that the formulation requires less plasticizer than those utilizing DNT allowing these negative energy materials to be compensated by the addition of more NC in the formula.

Example 5 depicts in Table 5 another single base propellant that does not contain either Dinitrotoluene (DNT) or Dibutyl-phthlate (DBP). DNT and DBP as indicated are the two ingredients currently used in the M1 propellant that are considered as carcinogens and toxic materials. Table 5 shows a comparison of the formulas of Example 5 (PAP 7993) and a batch of M1 material. A non-toxic, citrate type plasticizer Acetyl-triethyl-citrate (ATEC) was selected as replacement for DNT and DBP. The first pilot propellant sample (Example 5) was manufactured at a pilot plant using a conventional ether/alcohol solvent system. The samples were characterized for their stability, density, and burning rate characteristics. Based on the test results, the M1 modified formulation PAP 7993 had similar burning characteristics to the as M1 propellant and its energy content was also comparable with relative force of 97% of the M1 reference lot RAD92C071664. It is believed that the slightly lower energy content of the composition of Example 5 (DNT, DBP, DPA free) can be compensated by increasing the charge weight in the case to give equivalent performance compared to M1 propellant.

TABLE 5

PROPELLANT COMPOSITION (Example 5 -PAP 7993)		
CONSTITUENT	PERCENT EXAMPLE 5 (7993)	PERCENT RAD92C071664 M1
Nitrocellulose (NC) (13.15%N)	88.00	85.00
Acetyltriethyl Citrate (ATEC)	10.00	
EC	1.00	
KN	1.00	
Dinitrololuene (DNT)		10.00
Dibuylphthalate (DBP)		5.00
TOTAL	100.00	100.00
Diphenylamine (DPA)		1.00
GRAPHITE GLAZE		1.00
Impetus (J/g)	932	929
Flame temp (K)	2583	2522
Dimensions:	PAP 7993	RAD92C071664
Grain length	0.252	0.221
Grain diameter	0.050	0.052
Perf diameter	0.015	0.020
Web	0.018	0.016
Density (g/cc)	1.56	1.57
Vacuum Stability	1.21(ml gas)	
Closed Bomb results:		
Coefficient	0.00223	0.00874

Pressure exponent	0.742	0.831
RQ	92.47	100.00
RF	97.04	100.00
12,000 psi	2.366	2.147
14,000	2.647	2.424
16,000	2.929	2.714
18,000	3.178	2.987
20,000	3.46	3.284

Table 6 shows the ballistic firing results of the new formulation PAP 7993 in the XM231 charge configuration for the 155 mm Howitzer. These data show that the new formulation meets all of the requirements for the XM231 charge.

TABLE 6

TEST RESULTS FOR 155MM HOWITZER FIRINGS IN THE XM231 CONFIGURATION

		M1, 1-perf, 0.016" web, 2.90 lbs		PAP7993, 1-perf, 0.018" web, 3.10 lbs		PAP7993, 7-perf, 0.019" web, 3.50 lbs		M1, 7-perf, 0.025" web, 3.75 lbs	
	Charge Temperature	Muzzle Velocity (mps)	Maximum Pressure (kpsi)	Muzzle Velocity (mps)	Maximum pressure (kpsi)	Muzzle Velocity (mps)	Maximum Pressure (kpsi)	Muzzle Velocity (mps)	Maximum Pressure (kpsi)
Charge-1	-51°C (-60°F)	292.0	8.3	280.6	8.1	301.4	8.1	300.7	7.3
	+21°C (+70°F)	285.0	8.9	287.5	9.1	309.5	9.1		
	+63°C (+145°F)	298.1	9.3			314.1	9.7		
Charge -2	-51°C (-60°F)	415.6	19.1			451.0	19.9		
	+21°C (+70°F)	421.4	21.1			453.2	22.2		
	+63°C (+145°F)	424.0	23.4	424.3	22.7	461.3	23.3	461.8	19.7

This invention has been described herein in considerable detail in order to comply with the Patent Statutes and to provide those skilled in the art with the information needed to apply the novel principles and to construct and use embodiments of the example as required. However, it is to be understood that the invention can be carried out by specifically different devices and that various modifications can be accomplished without departing from the scope of the invention itself.

What is claimed is: